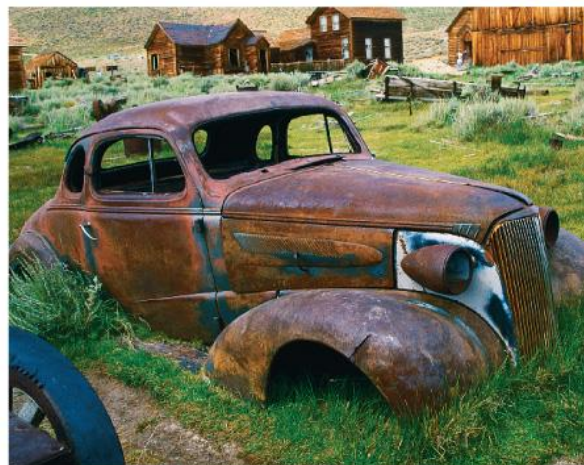# Spontaneity, Entropy, and Free Energy (Day One)

SFSU

CHEM 215

M. Corcoran
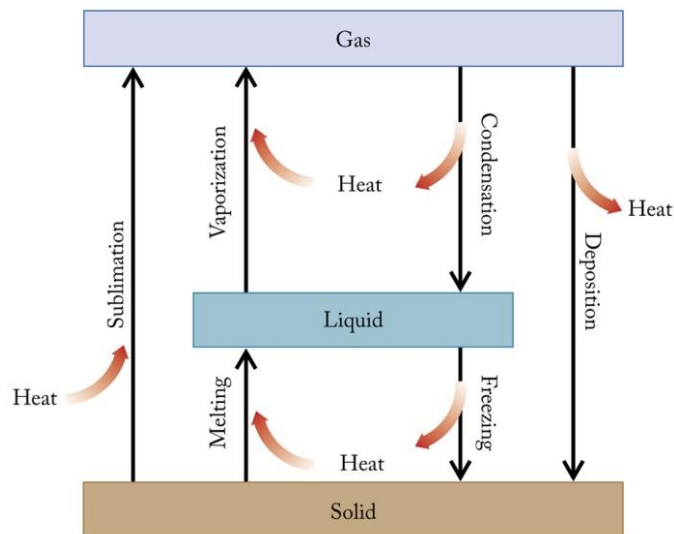

Spontaneous   Nonspontaneous

Definitions

- Thermochemistry – the study of heat changes (q) during a chemical reaction or physical change (CHEM 115)
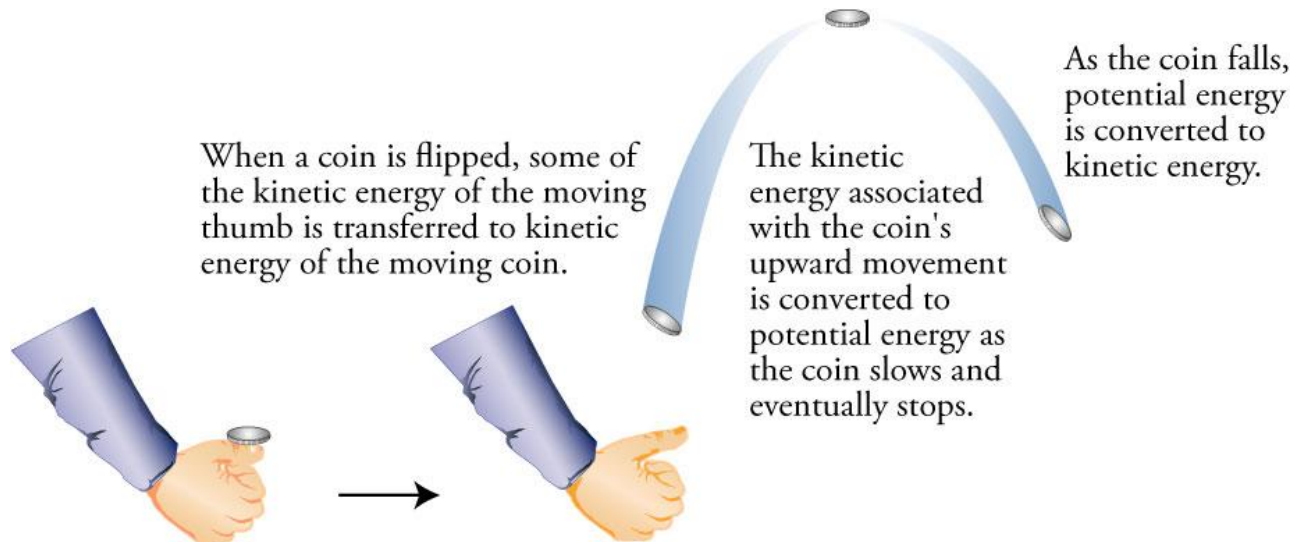

Chemistry: The Science in Context 3/e Figure 5.12
© 2012 W. W. Norton & Company, Inc.

- Thermodynamics – the study of energy changes and its transformations (CHEM 215)
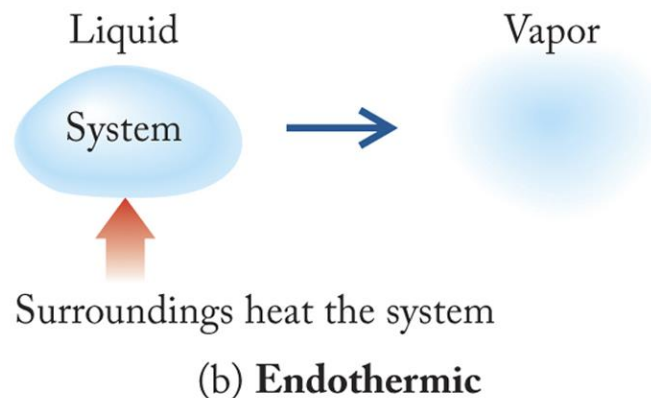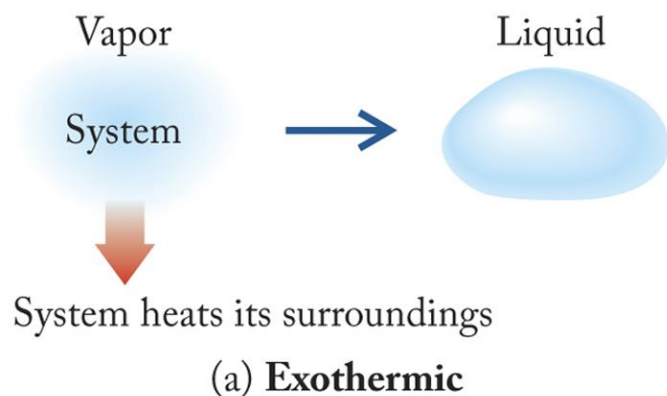
The Nature of Energy

- <u>Law of Conservation of Energy (first law of Thermodynamics)</u> energy can neither be created nor destroyed, but it can be converted from one form to another in physical and chemical processes and transferred from one system to another.

- In other words, *the energy of the universe is constant!*

When a coin is flipped, some of the kinetic energy of the moving thumb is transferred to kinetic energy of the moving coin.

The kinetic energy associated with the coin's upward movement is converted to potential energy as the coin slows and eventually stops.

As the coin falls, potential energy is converted to kinetic energy.

REVIEW Transferring Energy: System vs. Surroundings

- At constant pressure, $\Delta H = q$, the heat released or absorbed.
- <u>Transfer of energy is from the perspective of the system</u>
- <u>Exothermic</u> – Heat energy is released by the system.
- <u>Endothermic</u> – Heat energy is absorbed by the system.

Vapor   Liquid

System

System heats its surroundings

(a) **Exothermic**

Liquid   Vapor

System

Surroundings heat the system

(b) **Endothermic**

REVIEW Transferring Energy: System vs. Surroundings
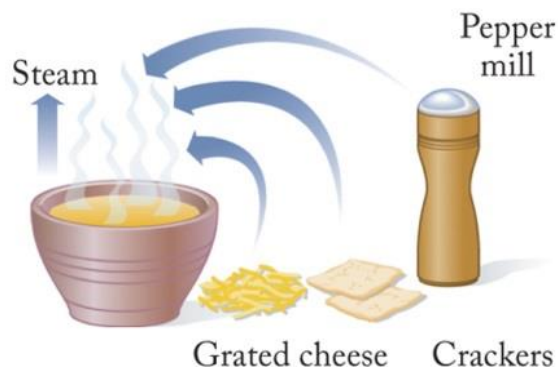
- <u>System</u> – is defined as the chemicals undergoing reactions or physical change.
  - For example $H_2O(l) \rightleftharpoons H_2O(g)$
- <u>Systems</u>: Isolated, closed and open.

Steam

Pepper mill

Grated cheese   Crackers

(a) **Isolated system:** A thermos bottle containing hot soup with the lid screwed on tightly

(b) **Closed system:** A cup of hot soup with a lid

(c) **Open system:** An open cup of hot soup

Transferring Energy: System vs. Surroundings

- <u>Reverse the reaction and reverse the direction of energy change</u>
- <u>Endothermic</u> (heat energy absorbed by the system) in one direction becomes <u>Exothermic</u> (heat energy released by the system) in the other direction.

(a) Solid   (b) Liquid   (c) Gas

$$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$$
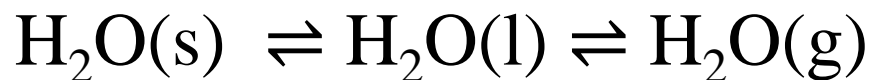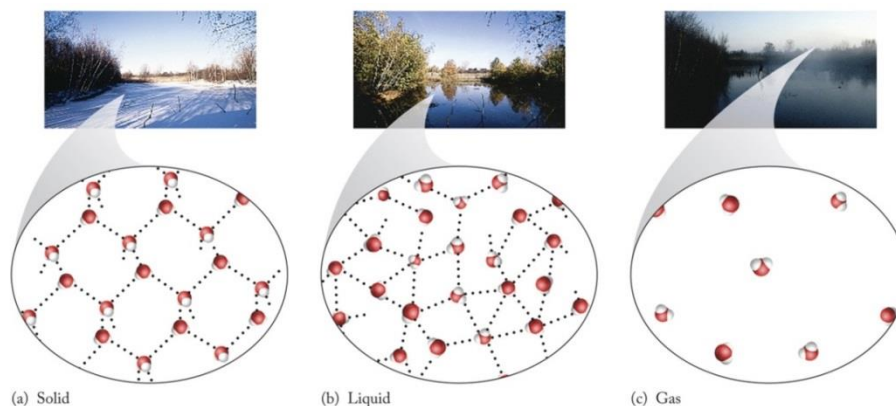
Endothermic⟶   ⟵ Exothermic

Thermodynamics Spontaneous Processes

- Does ice melt spontaneously when left out on the kitchen counter? The answer is yes unless your kitchen is at or below 0°C.
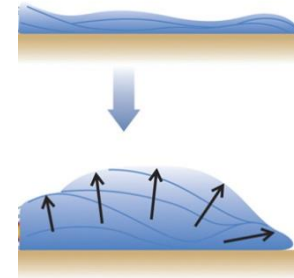 - $H_2O(s) \rightarrow H_2O(l)$ at room temperature
- Will a balloon inflate spontaneously?
  - No, it requires work
- Will the same balloon deflate spontaneously if there is a hole in it? Yes.
- **Spontaneous process – a process that occurs without outside intervention.**
- Nonspontaneous process – a process that occurs only as long as energy is continually added to the system

Spontaneity is *not* a synonym for exothermic

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) + energy$
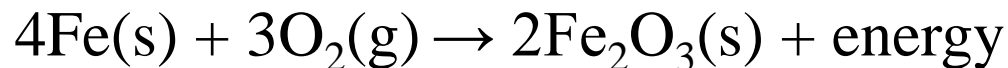
Iron rusting is exothermic ($\Delta H<0$) and the reaction between baking soda and vinegar is endothermic ($\Delta H>0$), yet BOTH PROCESSES ARE SPONTANEOUS!
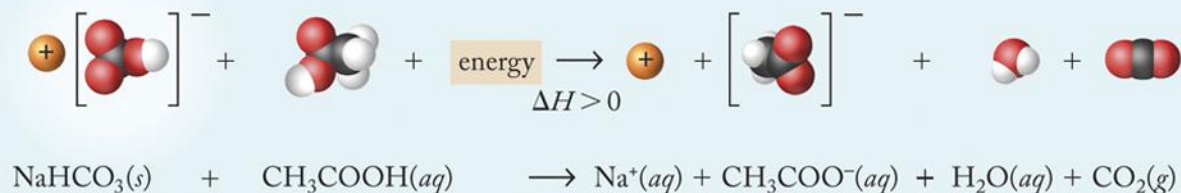
Entropy and the Second Law of Thermodynamics

- Entropy (S) – a measure of the distribution of energy and matter at a specific temperature.

- Second law of thermodynamics – the total entropy of the universe increases in any spontaneous process ($\Delta S_{univ} > 0$)

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{syst}$$

Spontaneous process MUST result in an increase in entropy of the universe! Second law of thermodynamics

| TABLE 14.1		Spontaneity of Reaction as a Function of ΔS_{sys} and ΔS_{surr}	
ΔS_{sys}	ΔS_{surr}	Spontaneity of Process	Reference
>0	>0	Always spontaneous	Figure 14.9(a)
<0	>0	Spontaneous if $\lvert \Delta S_{sys} \rvert < \lvert \Delta S_{surr} \rvert$	Figure 14.9(b)
		Nonspontaneous if $\lvert \Delta S_{sys} \rvert > \lvert \Delta S_{surr} \rvert$	Figure 14.9(e)
>0	<0	Spontaneous if $\lvert \Delta S_{sys} \rvert > \lvert \Delta S_{surr} \rvert$	Figure 14.9(c)
		Nonspontaneous if $\lvert \Delta S_{sys} \rvert < \lvert \Delta S_{surr} \rvert$	Figure 14.9(f)
<0	<0	Always nonspontaneous	Figure 14.9(d)

Chemistry: The Science in Context 3/e Table 14.1
© 2012 W. W. Norton & Company, Inc.
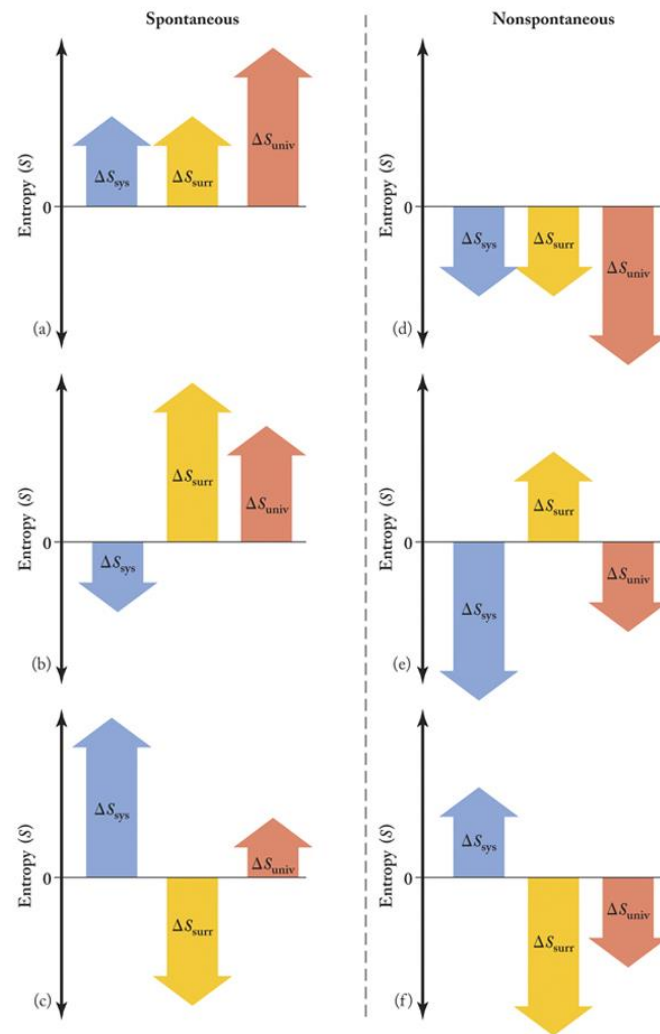
Chemistry: The Science in Context 3/e Figure 14.9
© 2012 W. W. Norton & Company, Inc.

Entropy, S

- Entropy, S, is the tendency to maximize dispersion of both matter and energy. Specifically, entropy is the measure of energy and matter that has spread out at a given temperature.

- IF energy and matter is spread out, the sign of ΔS is positive.

- Entropy can also be thought of as a measure of disorder or randomness.

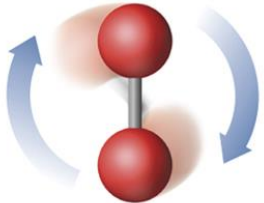- Which of the following has less order and more randomness?

(a) (b) (c) (d)
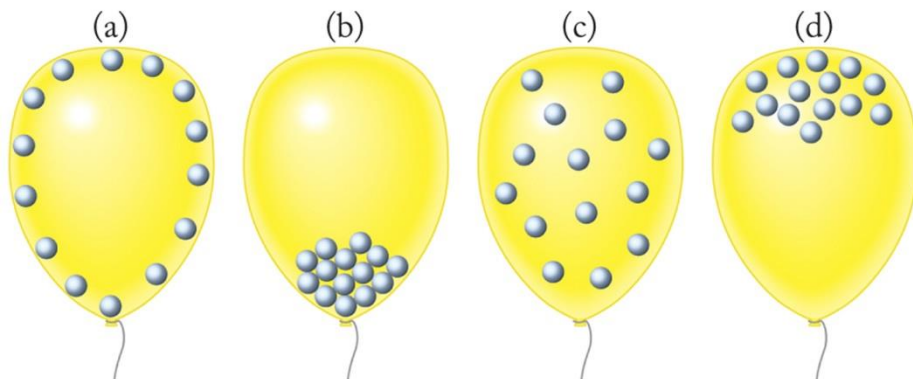
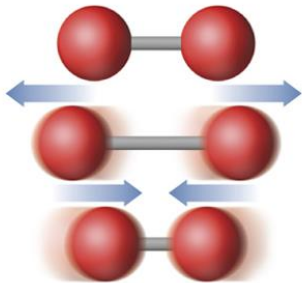# Types of Motion of Molecules: Example O_2
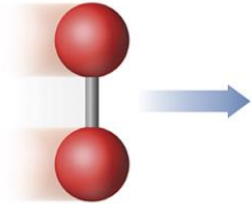
(a) Translational motion

Translational motion as the molecule travels from one location to another.

(b) Rotational motion

Rotational motion as the molecule spins around an imaginary axis perpendicular to the bond.

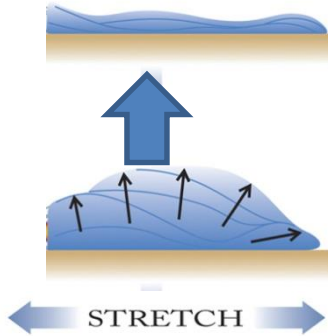(c) Vibrational motion

Vibrational motion as the two molecules move toward and away from one another

Chemistry: The Science in Context 3/e Figure 14.2
© 2012 W. W. Norton & Company, Inc.

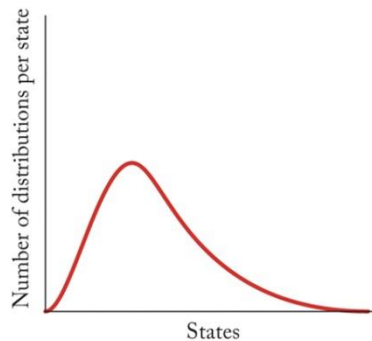The greater the thermal energy, the greater the type of motion.

Meaning of Matter "Spreading Out" in Terms of Energy

Why is this direction (deflation) spontaneous?

Energy levels for all types of motion are quantized.

As a matter spreads out, more energy levels or states become available.
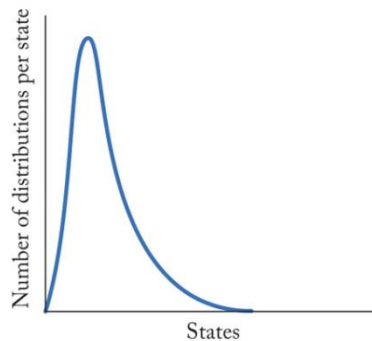
Energy becomes more dispersed and less localized because the molecules carrying it can be in a greater number of accessible energy levels.

STRETCH

Number of distributions per state

States

Number of distributions per state

States

(a)

(b)

Chemistry: The Science in Context 3/e Figure 14.5
© 2012 W. W. Norton & Company, Inc.

Freedom of Movement and Phase Changes

Case 1

Case 2

(a) Ice: primarily vibrational motion

(b) Liquid water: rotational and vibrational motion; some translational motion

(c) Water vapor: unrestricted translational, rotational, and vibrational motion
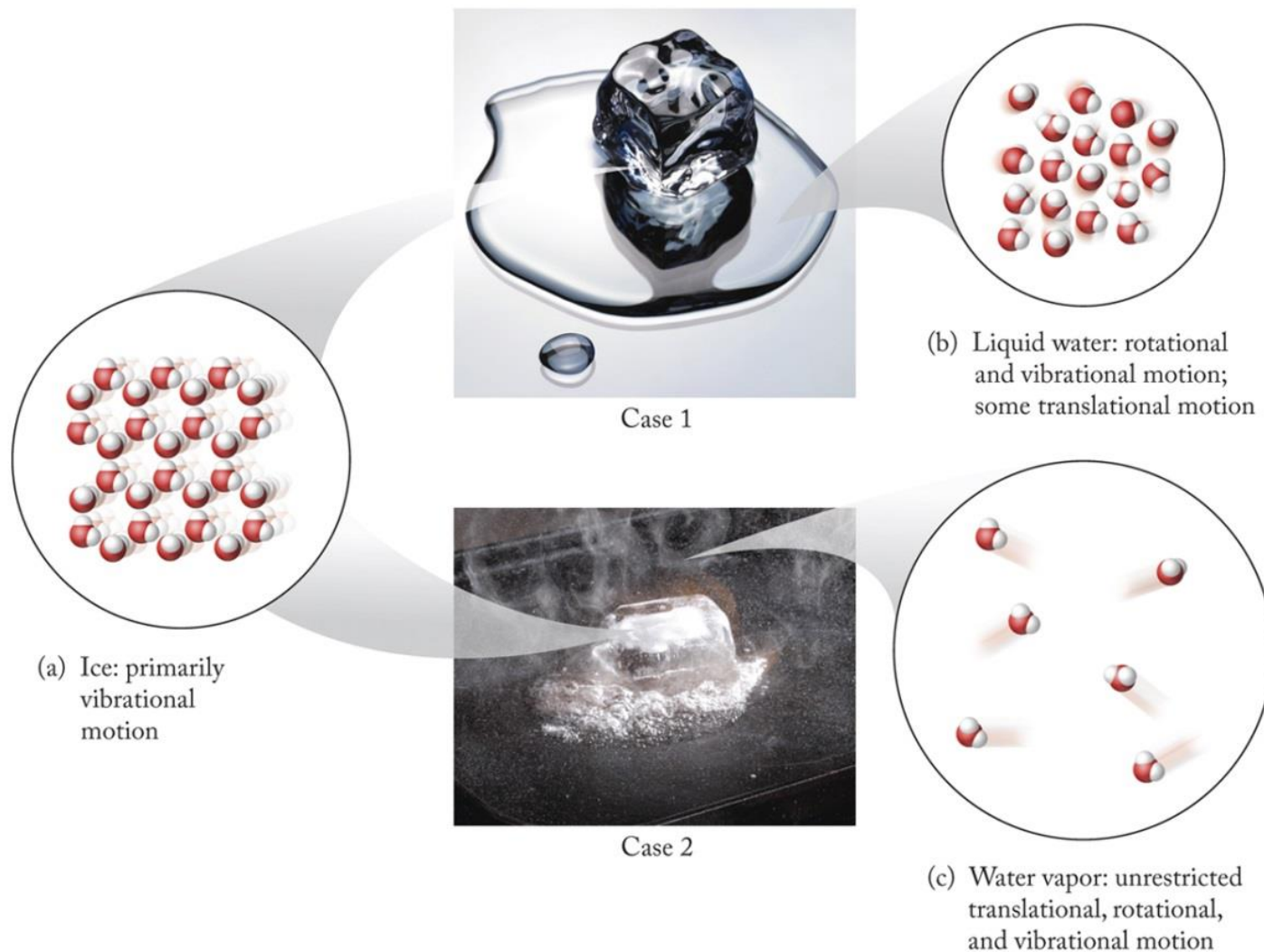
Phase Changes and Entropy, S
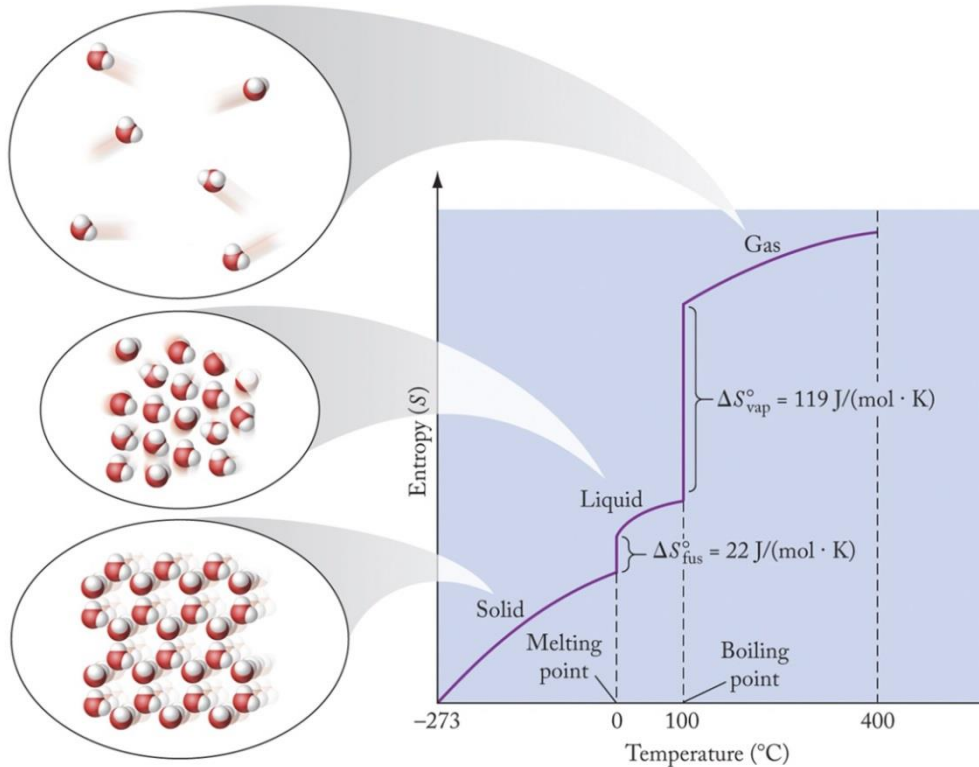
Chemistry: The Science in Context 3/e Figure 14.11
© 2012 W. W. Norton & Company, Inc.

Note: Don't worry about the non-linear nature of the heating curve.
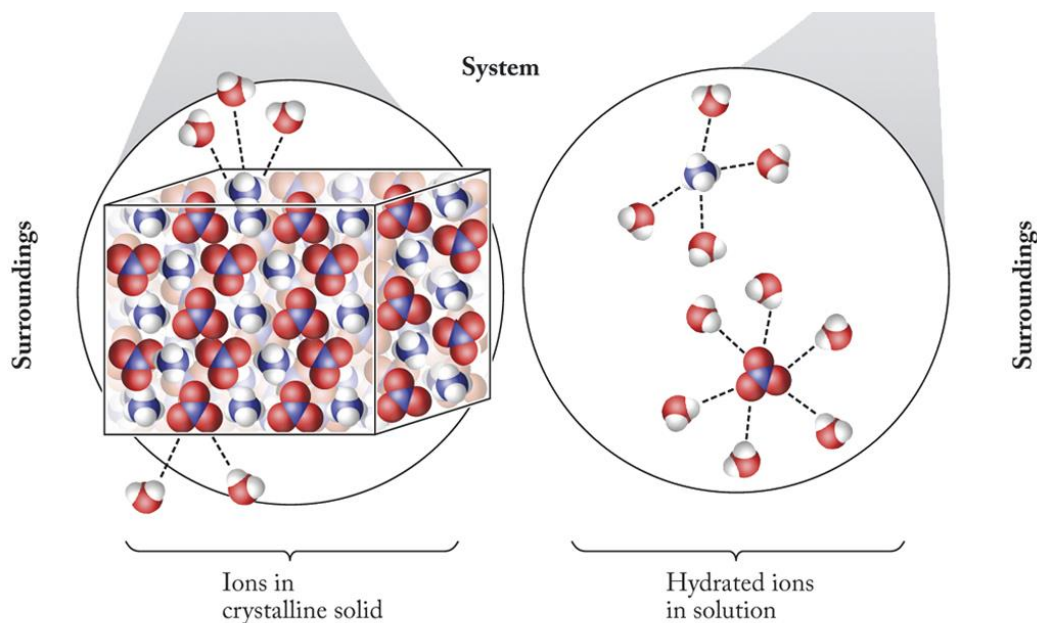
ΔS as ice is heated, ice melts (phase change), water is heated, water evaporates (phase change) and a water vapor is heated. Matter obviously becomes more dispersed with each phase change. And as T increases, KE increases which means greater motion and more dispersion of energy.

Freedom of Movement and Dissolution of NH_4NO_3

You saw in CHEM 115 lab that $\Delta H > O$ (endothermic) for the dissolution of NH_4NO_3 yet it was spontaneous. $\Delta S > O$ for this process (and any dissolution process) because there is an increase in the freedom of motion of the ions that make up the solid.

System

Surroundings

Surroundings

Ions in crystalline solid

Hydrated ions in solution

Chemistry: The Science in Context 3/e Figure 14.8
© 1987 Richard Megna, Fundamental Photographs, NYC

Freedom of Movement and DILUTION

Volume ($V_{initial}$) of stock solution

Multiply by molarity of stock solution ($M_{initial}$)

Moles of solute in stock solution = Moles of solute in diluted solution

Divide by total volume of diluted solution ($V_{diluted}$)

Molarity of diluted solution ($M_{diluted}$)

Chemistry: The Science in Context 3/e Figure 4.7
© 2012 W. W. Norton & Company, Inc.

Dilution of a concentrated salt solution by adding more solvent is a spontaneous process. $\Delta T \approx 0$, so $\Delta H \approx 0$, and $\Delta S_{surr} \approx 0$, so ΔS_{sys} is that that matters. ΔS_{sys} must be positive.

Both solvent and solute molecules are now dispersed in a larger volume,

Processes or Reactions for which $\Delta S_{sys} > 0$

- $H_2O(l) \rightarrow \mathbf{H_2O(g)}$
- $2H_2O(g) \rightarrow \mathbf{2H_2(g) + O_2(g)}$
- The **volume** of 1.0 mole of gas in 1.0 L is **expanded** to 2.0 L (with T constant)
- $CaCO_3(s) + \text{heat} \rightarrow CaO(s) + \mathbf{O_2(g)}$
- **Diluting** the 20.0 mL of a 1.0M NaCl solution to 100.0 mL.

For each of these processes in the *reverse* direction $\Delta S_{sys} < 0$

Summary of the Factors that Affect the Change of Entropy (ΔS)

- Entropy increases when
  - Temperature increases
  - Volume increases
  - The number of independently moving particles increases

iClicker Question

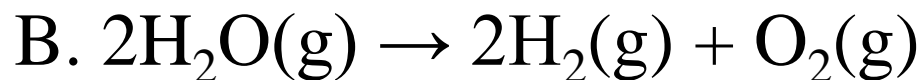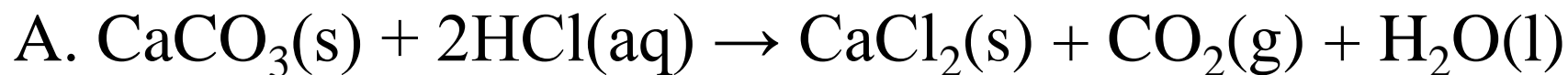Determine the sign of ΔS for the following reaction (T is constant): :

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$
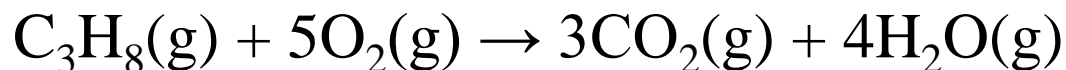
A. $\Delta S < 0$

B. $\Delta S > 0$

C. $\Delta S = 0$

Answer B. 6 moles of reactants form 7 moles of products.. Greater number of molecules and larger volume.

iClicker Question

For which of the following will $\Delta S_{sys} < 0$

A. $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(s) + CO_2(g) + H_2O(l)$

B. $2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$

C. The volume of 1.0 mole of gas in 2.0 L is compressed to 1.0 L (with T constant)

D. Both A and B

Entropy and Molar Mass

CH$_4$ — 186 J/mol K
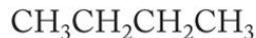
CH$_3$CH$_3$ — 230 J/mol K

CH$_3$CH$_2$CH$_3$ — 270 J/mol K
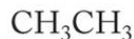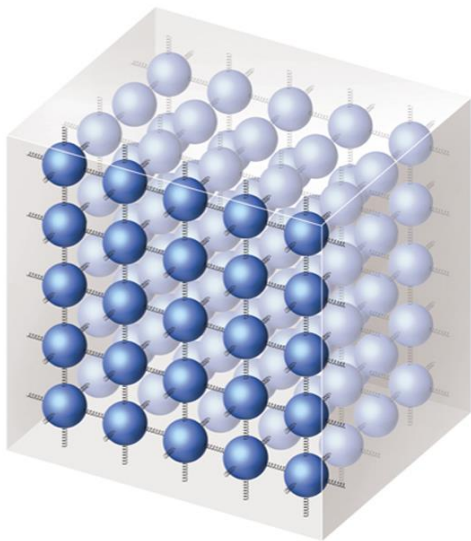
CH$_3$CH$_2$CH$_2$CH$_3$ — 330 J/mol K

Standard molar entropy increases with increasing molar mass.

The greater the number of bonds in a molecule means that there are different ways the molecule can move (bend, stretch, etc.)

Standard entropy also increases with decreasing rigidity of allotropes (different elemental forms of the same element). For instance, C$_{diamond}$ is more rigid than C$_{graphite}$, thus it has a lower standard entropy.

C$_{diamond}$(s)	2.4
C$_{graphite}$(s)	5.7

Third Law of Thermodynamics

(a) Perfect crystal at 0 K:
$S = 0$

All particles in exact
positions; all positions
occupied

Chemistry: The Science in Context 3/e Figure 14.10
© 2012 W. W. Norton & Company, Inc.

The entropy of a perfect crystalline solid is zero at absolute zero (0K).

Setting S=0 at 0K allows S to be determined at 298 K (recall the value of H cannot be determined, only ΔH)

TABLE 14.2   Selected Standard Molar Entropy Values[a]

Formula	$S°$, J/(mol · K)	Formula	Name	$S°$, J/(mol · K)
$Br_2(g)$	245.5	$CH_4(g)$	Methane	186.2
$Br_2(\ell)$	152.2	$CH_3CH_3(g)$	Ethane	229.5
$C_{diamond}(s)$	2.4	$CH_3OH(g)$	Methanol	239.9
$C_{graphite}(s)$	5.7	$CH_3OH(\ell)$		126.8
$CO(g)$	197.7	$CH_3CH_2OH(g)$	Ethanol	282.6
$CO_2(g)$	213.8	$CH_3CH_2OH(\ell)$		160.7
$H_2(g)$	130.6	$CH_3CH_2CH_3(g)$	Propane	269.9
$N_2(g)$	191.5	$CH_3(CH_2)_2CH_3(g)$	n-Butane	310.0
$O_2(g)$	205.0	$CH_3(CH_2)_2CH_3(\ell)$		231.0
$H_2O(g)$	188.8	$C_6H_6(g)$	Benzene	269.2
$H_2O(\ell)$	69.9	$C_6H_6(\ell)$		172.9
$NH_3(g)$	192.5	$C_{12}H_{22}O_{11}(s)$	Sucrose	360.2

[a] Values for additional substances are given in Appendix 4.

Gibbs Free Energy, ΔG

Given: $\Delta S_{univ} = \Delta S_{surr} + \Delta S_{syst}$

- Derive the equation $\Delta G = \Delta H - T \Delta S$
- For any spontaneous process, the sign of ΔG will be negative.
- For any nonspontaneous process, the sign of ΔG will be positive.
  - Both ΔH and ΔS are necessary to determine spontaneity

TABLE 14.4 Effects of ΔH, ΔS, and T on ΔG and Spontaneity

	SIGN OF		
ΔH	ΔS	ΔG	Spontaneity
$-$	$+$	Always <0	Always spontaneous
$-$	$-$	<0 at lower temperature	Spontaneous at lower temperature
$+$	$+$	<0 at higher temperature	Spontaneous at higher temperature
$+$	$-$	Always >0	Never spontaneous